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(71) Applicant: THE REGENTS OF THE UNIVERSITY OF CALIFORNIA [US/US]; 2199 Addison Street, Berkeley, CA 94720 (US).

(72) Inventor: KUNBARGI, Hassan ; 6175 Canterbury Drive, Apt. No. 104, Culver City, CA 90230 (US).

(74) Agents: ROSE, Alan, C. et al.; Poms, Smith, Lande & Rose, 1888 Century Park East, Suite 1000, Los Angeles, CA 90067-1773 (US).

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(54) Title: USE OF CEMENT KILN DUST AND RED MUD TO PRODUCE HYDRAULIC CEMENT

(57) Abstract

A high iron content cement is formed principally from two industrial by-products which are available in very large quantities, (1) cement kiln dust, or CKD, and (2) the Red Mud which is a by-product of the extraction of alumina from bauxite ore. Smaller quantities of lime (calcium oxide) and gypsum (calcium sulfate) and aluminum oxide as needed, are added to the CKD and Red Mud, and the mixture is heated to between about 1250 degrees C. and 1400 degrees C., substantially lower than the kiln temperature for Portland cement. The resultant clinker is pulverized to form a lightweight, fast setting, strong, hydraulic cement.

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USE OF CEMENT KILN DUST AND RED MUD TO PRODUCE HYDRAULIC CEMENT

Field of the Invention

This invention relates to a method of making a special form of cement, differing significantly from Portland cement, and having a relatively high iron content, and to the resultant cement and concrete.

Background of the Invention

The present invention involves, as an important aspect thereof, the making of cement from two materials which are available in very large quantities as waste by-products of (1) the cement industry and (2) the aluminum industry. More specifically, these waste materials are Cement Kiln Dust, better known as CKD, and the "Red Mud" which remains as a residue in the course of the process of extracting aluminum from the aluminum-containing ore, bauxite. The nature of the processes by which CKD and Red Mud are produced as undesired by-products will therefore be briefly reviewed.

Process of Making Conventional Cement

Cement such as Portland cement is the product of reaction at high temperature (in the order of 1400 degrees C. to 1600 degrees C.) of (a) an argillaceous material such as clay, containing substantial proportions of silicon oxide, or silica, and aluminum oxide or alumina, and (2) a calcareous material such as lime, which is formed principally of calcium oxide. After the two materials are prepared in fine powders and mixed, they are heated and fused in a big long rotary kiln, to form clinker. The kilns are slightly tilted, with raw materials being fed in at the upper cooler end, and the fused product or clinker being received from the lower, hot end. Hot gases flowing in the opposite direction,

from the low end of the rotary kiln to the high end, carry the "CKD" or cement kiln dust out of the kiln, where it is separated from the gas stream by filters or precipitators. The clinker is ground and used as cement. Gypsum, or calcium sulfate, may be added and blended to the cement at this point in the process to control the setting time of the cement.

For the purpose of clarifying terminology, it may be noted that sand is added to the Portland cement, and normally gravel is also added and of course a proper proportion of water. The resultant Portland concrete takes a substantial period of time to set up, and reaches a substantial level of its final strength in about a month. When cement is mixed directly with water, it may be referred to as a paste; and when it is mixed with sand but not gravel, it may be referred to as mortar.

Now, a certain amount of the collected CKD may be fed back into the process with the pulversized raw materials. However, the sodium and potassium alkali content of the collected CKD tends to build up, in view of the lower melting point of sodium and potassium oxides; and it creates a problem when this alkali content, in terms of sodium and/or potassium alkali oxides, exceeds about 0.6 percent or one percent, because of the resultant lowering of the fusion temperature of the material being processed. This reduces the thickness of the layer of material coating and protecting the refractory lining of the kiln. In addition, the higher percentages of sodium and potassium alkalis in the Portland cement being processed results in the formation of free lime, which may eventually cause concrete to crack, because it expands in the presence of water.

For one year, 1972, in which a study was made, it was determined that 5,000,000 tons of CKD were discarded. The common method of disposing of CKD is in surface piles or in abandoned quarries.

"Red Mud" From Aluminum Extraction

Bauxite is the ore which is most widely used as a source of aluminum. Aluminum oxide is present in bauxite in an amount equal to about 60 percent or 65 percent. As one step in the processes for extracting aluminum oxide from bauxite, some of the aluminum oxide is leached from the crushed bauxite ore, with hydrochloric acid and sodium chloride often being used, and the solid residue from the leaching step or steps is known as "Red Mud", or "Brown Mud", with different sources of aluminum ore and slightly different processes giving a residue of somewhat different colors. In the present specification and claims, the phrase "Red Mud" with initial capital letters will refer to this type of by-product material, whether red in color or brown. The production of Red Mud is more than 5,000,000 tons per year; and it has been estimated that approximately ninety million tons have been accumulated in settling ponds.

Summary of the Invention

In accordance with a broad aspect of the invention, it has been determined that an excellent cement may be formed from the two waste products, (1) cement kiln dust, CKD, and (2) "Red Mud", combined with the addition of (3) sulfur containing material, such as gypsum, calcium sulfate. Further, if the alumina, or aluminum oxide content of the Red Mud is low, it may be supplemented by the addition of more (4) alumina or aluminum oxide. Also, depending on the calcium oxide content of the CKD and Red Mud, some (5) calcareous material such as lime may be added to the mixture.

These raw materials are finely divided and intimately mixed, and thereafter may be processed in a rotary kiln or in a comparable heating process at somewhat lower temperatures, such as 1250 degrees C. to 1350 degrees C.,

with no need to exceed 1400 degrees C. The resulting clinker may be pulverized as in the case of conventional Portland cement.

The resultant concrete has excellent strength, with its compressive strength being greater than concrete made from Portland cement, and in some cases comparative compressive strength tests showed the new concrete to be more than fifty percent (50%) stronger than Portland concrete.

It is further noted that the presence of high levels of sodium and/or potassium alkalis in the CKD does not have an adverse effect on the new cement, unlike the case of Portland cement. The explanation for this difference is believed to be as follows. In the case of Portland cement, these monovalent alkalis compete for water with the calcium silicate, and prevent the reaction involving the hydration of calcium silicate from going forward, in addition to interference with the kiln process as noted above. In the new process, however, the hydration of calcium aluminum ferrite and calcium aluminum sulfate, goes forward rapidly and the concrete hardens rapidly, and the competition of the sodium and potassium alkalis with calcium oxide for water does not cause any problem or weaken the concrete.

Additional advantages of the new cement include the reduced manufacturing cost resulting from the lower temperature of fusion, the slightly lighter weight of the new cement, and the very rapid setting time of the new cement. It is also believed that the higher iron content of the new cement provides improved bonding with the steel reinforcing widely used in concrete, and accordingly increases the strength of reinforced concrete structures.

The prior work of Povinder K. Mehta as set forth in U.S. Patent No. 4,036,657, granted July 19, 1977 is of interest in disclosing a "High Iron Oxide Hydraulic

Cement". Some of the cements disclosed in the Mehta patent are similar to the resulting cements achieved in accordance with the present invention by using the waste products CKD and Red Mud. As starting materials, the Mehta patent does suggest the possible use of bauxite as a source of aluminum oxide, and for iron oxide the possible use of industrial waste products such as flue dust from iron and steel plants. However, the Mehta patent does not suggest the use of either CKD or Red Mud. Accordingly, one important aspect of the present invention involves the method of making high iron content cements principally from these plentiful waste products.

In accordance with another aspect of the invention, it was determined that Red Mud had the desired high iron content for the formation of cements of the type disclosed in the Mehta patent; and in accordance with a further aspect of the invention it was determined that the high alkali content of cement kiln dust surprisingly did not adversely affect the properties of the cement, unlike its effect on Portland type cements, as discussed above.

In addition to the major constituents of (1) Red Mud and (2) CKD, it is desirable to add lesser quantities of additional materials. Since CKD and Red Mud do not have the proper amount of sulfur tri-oxide for a strong high iron type cement, some sulfur containing material such as gypsum should be added. Additional calcium oxide in the form of lime is often needed, depending on the calcium oxide content of the CKD and Red Mud. Depending on the levels of concentration of aluminum oxide in the Red Mud, additional aluminum oxide may also be added.

For completeness, one typical schedule of CKD components, Red Mud components and a preferred composition of the cement of the present inventions will be set forth below, in Tables I for CKD, Table II for Red Mud and Table III for the starting materials and

composition of one cement illustrating the present invention.

Incidentally, it may be noted that whereas the gypsum is added after the clinker has been formed to regulate setting time in the case of Portland cement, it may form part of the clinker in the present case.

TABLE I

ANALYSIS OF CKD EMPLOYED IN THE PRESENT EXAMPLE

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI.
Weight %	10.6	-3.2	1.6	50.3	1.9	0.4	3.8	27.9

TABLE II

CHEMICAL ANALYSIS OF RED MUD USED IN THE PRESENT EXAMPLE

Material	Weight %
Moisture	13.4
Al_2O_3	14.75
Fe_2O_3	46.25
SiO_3	4.17
CaO	8.84
TiO_2	5.86
P_2O_5	1.41
Na_2O	1.85
ZnO	0.58
SO_4	0.58
LOI	13.42

TABLE III

Raw Materials	Weight %	Oxide	Weight %
CKD	25%	CaO	36.6%
Red Mud	28%	Al_2O_3	17.9%
Calcium Oxide CaO	13%	Fe_2O_3	13.35
Calcium Sulfate $CaSO_4$	21%	SiO_2	3.7%
		SO_3	12.5%
Alumina	13%	Na_2O	0.6%
		TiO_2	1.65%
		K_2O	0.95%

Raw Materials and Related Oxides After "LOI", Loss on Ignition or Firing.
See Table No. VI for Raw Materials Before "LOI"

It is, of course, to be understood that the proportions set forth herein illustrate the presently preferred proportions based on the limited number of examples as detailed below in the body of the specification. In some cases where the composition of the CKD and Red Mud differ, the additional materials to be added would also differ. Thus, for example, in the process whereby Red Mud is obtained as aluminum oxide is leached from bauxite, in some cases lesser amounts of the initial quantity of aluminum present in bauxite may be removed from the bauxite; and in this case the Red Mud would have more residual aluminum oxide, and less additional aluminum oxide would have to be added to the cement.

More generally, ranges of proportions of the major constituents based on the limited number of tests performed up to the present time and as detailed below, are set forth in Table IV.

TABLE IV

COMPOSITION RANGES OF NEW CEMENT ILLUSTRATING THE PRESENT INVENTION

Oxides	Range A	Range B	Range C
CaO	32% - 40%	30% - 65%	20% - 70%
Al_2O_3	15% - 20%	10% - 25%	5% - 35%
Fe_2O_3	10% - 16%	8% - 20%	5% - 25%
SiO_2	2% - 5%	1% - 10%	0% - 20%
SO_3	10% - 15%	5% - 20%	4% - 25%

Figures Are Weight Percentages After "LOI" or Loss on Ignition or Firing.

Concerning Table IV set forth hereinabove, the following points may be noted:

1. Red Mud and CKD are used in quantities of at least 20% each.

2. Alumina may be added to increase the Al_2O_3 content of the mixture, but may not be necessary if the alumina content of the Red Mud is high.

3. Lime may be used to provide additional CaO but may not be necessary if the CaO content of the Red Mud is high.

4. Monovalent Alkalis such as Sodium and Potassium Oxide are normally present in CKD and Red Mud such that the combined percentage of these oxides is greater than 0.5% and may be as much as 1% or 2%, but normally not over 5% and certainly not over 10%.

5. The SO_3 may be added in the form of gypsum.

6. The percentages set forth in Range A of Table IV are to be preferred; the percentages of Range B are somewhat broader; and the percentages of Range C constitute an even broader range illustrating the principles of the invention.

Other objects, features and advantages of the invention will become apparent from a consideration of the following detailed description and from the drawings.

Brief Description of the Drawings

Figure 1 shows some of the grayish, chocolate colored, brownish cement powder formed in accordance with the invention;

Figure 2 shows some small test blocks of mortar made from the cement of Figure 1; and

Figures 3 and 4 are perspective and cross-sectional views, respectively, of a lightweight reinforced concrete beam with an enhanced bond between the high iron concrete of the present invention and the reinforcing steel.

Detailed Description of the Preferred Embodiments

Referring more particularly to the drawings, Figure 1 shows three tapered test cubes of hardened mortar made using cement having the composition set forth in TABLE III. Further, the fine powder shown in Figure 2 is finely ground clinker having the composition set forth in TABLE III. The mortar used in forming the cubes of Figure 1 was made of a ratio of 2.75 parts of sand, and one-half part water by weight, to one part of cement.

The results of compressive strength tests on mortar samples, according to ASTM No. C109 testing procedures is as follows:

TABLE V

Time	1 day	7 days	21 days
Sample 1 (new)	2310 psi	3010 psi	3595 psi
Sample 2 (new)	2450 psi	3375 psi	3938 psi
Average	2380 psi	3193 psi	3767 psi
Portland cement	0 - Very Low	1700 psi	2400 psi

In the foregoing table the figures for Samples 1 and 2 were from actual measurements, and the figures for

Portland cement were from texts.

Figure 3 is a perspective view of a double-T section steel reinforced concrete beam, and Figure 4 is a cross section taken through the beam of Figure 3, showing the longitudinally extending steel prestressing strands, and the transversely extending steel stirrups. The high iron content cement of the present invention will bond more intimately with the steel reinforcing, and this factor, together with the lighter weight and increased strength of the new cement, will make for improved reinforced concrete structures, having either greater strength, or less concrete to provide the same strength.

It is further noted that X-ray diffraction tests indicate the presence of calcium aluminosulfate, as well as the presence of its hydrate, known as Etringite. Calcium aluminosulfate is slightly expansive, as compared with conventional Portland cement which shrinks slightly as it cures. Accordingly, by combining the new type of cement with conventional Portland cement, the shrinkage of Portland cement may be at least minimized, and using the proper proportions, a cement with substantially no change in dimensions on curing may be achieved. As of the present date, exact figures on changes in dimensions, if any, of the new cement in the course of curing have not been developed.

Incidentally, the cubes which had high compressive strength test results were formed in enclosed chambers formed by bolting two machined parts together, and opening the mold after one day. In view of the rapid setting and high initial strength of the new cement, it appears possible that self pre-stressing may have occurred as a result of the expansive components included in the new cement.

EXAMPLE I

In the formation of the cement discussed above, the following steps were taken: A batch was prepared con-

taining: 800 g. of CKD, 882 g. of Red Mud, 375 g. of lime, 500 g. of gypsum and 300 g. of alumina, which were mixed by ball milling for 1/2 hour. CKD was used directly, while red mud had to be sieved through a 100 mesh sieve, in order to exclude large agglomerates present among the fine powder.

The materials included in this first batch are set forth in tabular form below, in TABLE VI, which is equivalent to TABLE III but prior to "LOI", or Loss on Ignition, or loss in the course of firing.

TABLE VI

	Grams	Percent
CKD	800	28%
Red Mud	882	30.87%
Lime	375	13.13%
Gypsum	500	17.5%
Al_2O_3	300	10.5%
	2857 grams	100 %

Analysis of Material

Before "L.O.I." (Loss on Ignition or firing).

Clinkering and Cooling:

After mixing, the charge was put into fire clay crucibles and put into an electric furnace; the temperature was then raised to 1350 degrees C. and held there for half an hour. Partial fusion was found to have occurred when the crucibles were taken out and cooled. Two methods of cooling the clinker were used, one by immersing the hot crucible in water, followed by blowing a stream of air on the surface of the crucible; in the other method the hot crucible was immersed completely in water. In the first method the cooling rate was slower than that of the second method. After cooling, the crucibles were broken and the clinker was ready for crushing and grinding.

Crushing and Grinding:

Primary pulverizing of the resulting clinker was carried out with a laboratory disc pulverizer. Fine grinding was provided by ball milling, using a rubber-lined mill and high-alumina balls. After 12 hours of ball milling, the resulting particle size distribution was determined, and is given in Table VII.

TABLE VII

Particle Size Distribution of Ball-Milled Clinker of the New Cement

Particle size (microns)	+150	-150 + 75	-75 + 53	-53 +45	-45
Weight %	1.1	7.0	10.2	36.6	44.7
Sieve No. U.S. series	100	200	270	325	Pan

NOTE: The numbers over the weight percentages indicate the range of particles in each weight percentage. Thus, 36.6% of the particles are between 45 and 53 microns; 44.7% less than 45 microns.

Evaluation of Properties of Cement Paste and Mortar

Strength in Flexure:

Rectangular bars of the new cement were formed by casting neat cement paste in plexiglass molds. The bar dimensions were 10 x 10 x 100 mm. Seven samples were made from the new cement, and seven samples from Portland cement also were made for comparison, using, in each paste, a cement/water ratio of 2/1 (weight), and a curing period of 24 hours in a saturated moist air environment. The bars were loaded in three-point bending, using a mechanical testing machine (Tinius Olsen) with separating distance between supporting points, L = 2".

Compressive Strength Test:

Compressive strength tests were carried on the new cement-sand mortar following the standard procedure of ASTM C109. In this testing, 2" cubes of cement-sand

mortar were formed. A standard silica sand was used, No. 30, and the sand/cement weight ratio was 2.75/1. The water/cement weight ratio was 1/2. Tests have been made for mortar after 24 hours in moist air, after one day in moist air and 2 days immersed in water, after one day in moist air and 6 days immersed in water, and after one day in moist air and 20 days immersed in water. The cured specimens were loaded in a Baldwin pneumatic testing machine. The compressive strength was made for two kinds of cement, the first one was the air cooled cement, and the second was the water cooled cement.

X-ray Diffraction of the New Cement:

X-ray diffraction was used to identify the main crystalline constituents of the powdered clinker; in addition, efforts were made to identify the chief crystalline products after setting (hydration) of the new cement. The X-ray target used was Cu-K with a Ni filter and 10^3 counts per second. The standard deviation of the counting was 1%, and with 2 degrees/minute scanning rate. The hydrated cement was cast in the plastic sample holder of the X-ray machine, and immersed in water for 6 days after 24 hours in moist air.

Summary of Results

The strength of the new cement mortar was substantially greater than the compressive strength of Portland cement as indicated in Table V, set forth above. Table VIII shows the relative flexure strength of the new cement and Portland cement after one day.

The color of the produced cement ranged from light chocolate brown to dark green, depending on the percentage of gypsum and lime which have been added. The major amounts of raw materials used were CKD, (about 35% weight), and Red Mud, (about 25% weight).

Summarizing the advantages of the new method and

the new cement, they include the following: (1) it provides a solution to a serious waste disposal problem in the cement and aluminum industries, (2) a high strength cement is produced for construction applications, (3) the raw materials for this cement are available for use, without any further grinding or treatment, in the manufacturing process, (4) the firing temperature of cement is lower than the firing temperature of Portland cement by 200-300 degrees C., (5) there is no need for adding any retarder to the clinker because the alkali problem will be solved during the clinkering processes, and the strength of the produced cement does not depend on the hardening of silica-gel. Thus, the total cost of manufacturing the new cement by clinkering CKD and red mud is more economically attractive than the cost of manufacturing Portland cement, due to the low cost of the raw materials, and to the energy saving in the preparation and firing processes of the cement clinker.

X-Ray Diffraction of the New Cement Clinker

The new cement clinker in its glassy phase was subject to X-ray diffraction examination. It appeared from the X-ray patterns for air cooled cement and for water cooled cement, and with reference to standard pattern tables of Portland cement, that the major constituents of the new cement are as follows:

TABLE VIII

FLEXURE STRENGTH OF THE NEW CEMENT AND PORTLAND CEMENT SPECIMENS

Portland Cement		New Cement	
Load (lb)	Modulus of rupture psi	Load (lb)	Modulus of rupture psi
20	1000	30	1500
21	1050	39	1950
30	1500	29	1450
21	1050	29	1450
28	1400	29	1450
20	1000	38	1900
19	950	30	1500
Ave. 23	1136	32	1600

TABLE IX

X-RAY DIFFRACTION OF THE NEW CEMENT CLINKER

C_4AF: [2.77, 2.63, 2.54, 2.43, 2.19 A° (d) values].
C_2F : [2.69, 2.07, 1.94, 1.84, 1.74 A° " "].
β-C_2S:[3.80, 3.37, 3.03, 2.87, 2.78 A° " "].
$C_4A_3\overline{S}$ [4.9, 3.75, 3.49, 3.24, 2.9, 2.65, 2.16]

TABLE X

THE CRYSTALLINE CONSTITUENTS
OF THE NEW HYDRATED CEMENT

C_4AH_{13}: [8.2, 4.1, 3.9, 2.9, 2.73 A° " "].
C_3AH_8 : [2.68, 2.70, 2.47, 2.31, 2.14 A° " "].
C_3FH_6: [2.72, 2.60, 2.50, 2.32, 2.06 A° " "].
$C_3A\ CaSO_4.3H_2O$ (Ettringite):[3.92, 3.03, 2.81, 2.57 A°].
C_2SH : [2.75, 2.67, 2.63, 2.44, 2.36 A° (d) values].

In the foregoing Tables IX and X, the special symbols employed in connection with cement and concrete work are used:

$A = Al_2O_3$, alumina, or aluminum oxide
$H = H_2O$, water
$C = CaO$, calcium oxide
$F = Fe_2O_3$, iron oxide
$S = SiO_2$, silica, silicon oxide
$\overline{S} = SO_3$, sulfur tri-oxide
$C_4A_3\overline{S}$ Calcium Alumina Sulfate

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In Table IX certain peaks have been shifted somewhat and are not exactly at the expected values. In addition, the role of the other constituents of the raw materials such as TiO_2, Mn_2O_5, P_2O_5, and ZnO, is not yet known.

II - The Crystalline Constituents of the New Hydrated Cement

Constituents of the hydrated cement after seven days of curing, were identified by analysis of the X-ray pattern. The major constituents of the hydrated cement are set forth in the associated Table X. It was observed that the peaks are shifted slightly, some of them are missing, and considerable over-lapping has occurred.

Compressive Strength Test ASTM C109, and Strength in Flexure:

The compressive strength results relating to the new cement in accordance with the test procedures of ASTM C109 were given hereinabove in Table V. The strength of flexure for new cement paste is given in Table VIII for both the new cement and for Portland cement, using a cement/water weight ratio of 2/1 and 24 hours curing in moist air.

In the foregoing portion of the specification the detailed tests which were made on one successful new high iron cement composition were set forth in some detail. In the remainder of the specification, some other compositions which were made but not elaborately tested will be briefly discussed.

EXAMPLE II

Cement was successfully formed from another somewhat different constituent materials having the following weight percentages (after LOI):

CKD	30%
Red Mud	20%
CaO	20%
Al_2O_3	15%
$CaSO_4$	15%

A process similar to the first example was followed, and firing was accomplished at about 1300 degrees C. Good cementitious action was observed. However, detailed tests of the precise mechanical properties have not been made.

For completeness, the results of a number of initial unsuccessful tests will also be included as follows:

EXAMPLE III

(A) Starting Materials:

CKD - 50% + Red Mud - 50%

(B) Calculated Chemical Constituents:

CaO	29.6%
Al_2O_3	9.00%
SiO_2	7.4%
Fe_2O_3	23.9%
Na_2O	1.1%

The foregoing and other percentages in the present specification are weight percentages (after LOI) unless otherwise specified.

A batch of 500 g. was mixed, using 250 g. CKD and 250 g. Red Mud. The mixture was blended in V-blender for one hour, then heated to 1250 C. in a fire clay crucible and sintered for one hour. The cooling process was handled by immersing the crucible wall in water, then blowing a stream of cooled air on the unwetted surface of the melt until it was possible to handle the warm crucible with bare hands. The mixture reacted with the crucible; therefore, the crucible had to be broken in

order to get the clinker out. The clinker was then crushed in a porcelain mortar and sieved through #325 mesh screen. About 50 g. of the crushed clinker which passed #325 sieve was mixed with water to form a paste which was cast in small dish and held in moist air for one day to determine the cementitious reaction. The clinker color was black, and when mixed with water it turned to gray. The cementitious reaction was determined by the indentation of finger nail in the paste, and if it was hard enough an iron nail was used. After one day in moist air there was a resistance for indentation, but when adding water the paste turned soft and muddy. Thus for composition III there was no cementitious reaction.

EXAMPLE IV

(A) Starting Materials:

CKD	70%	+	Red Mud	30%

(B) Calculated Chemical Constituents:

CaO	37.9%
Al_2O_3	6.7%
SiO_2	8.7%
Fe_2O_3	15.00%
Na_2O	0.83%

A batch of 200 g. was prepared using the same procedure as in composition III. But at 1250 C there was partial melting and there was no glass phase in the crucible. At 1350 C. there was a glass phase and the mixture was sintered for one hour at that temperature. Same results as for composition III. The clinker color of composition II was dark green and when mixed with water it turned to brown green. Also, there was no cementitious reaction.

EXAMPLE V

(A) Starting Materials:

CKD - 50%, + Red Mud - 30%, + CaO - 20% (as lime).

(B) Calculated Chemical Constituents:

CaO	47.8%
Al_2O_3	6.00%
SiO_2	6.5%
Fe_2O_3	14.7%
Na_2O	0.75%

Fired at 1300°C. Cementitious, but not stable when water was added after hardening. No strength.

EXAMPLE VI

(A) Starting Materials:

CKD - 30%, + Red Mud- 45% + CaO - 15%, + Al_2O_3 - 10%

(B) Calculated Chemical Constituents:

CaO - 34.00%, Al_2O_3 - 17.1%, SiO_2 - 5.06%, Fe_2O_3 - 21.3%, Na_2O - 0.95%.

Similar to Example V. The sintering temperature was 1300 C. The clinker color was yellow. Set up in one day.

EXAMPLE VII

(A) Starting Materials:

CKD - 30%, + Red Mud - 40%, + CaO - 15%, + Al_2O_3 - 15%,

(B) Calculated Chemical Constituents:

CaO - 33.6%, Al_2O_3 - 21.9%, SiO_2 - 4.9%, Fe_2O_3 - 19.00%, Na_2O - 0.86%.

Similar to Example VI, but there was a dust on the paste after drying. Slightly harder than Example VI.

EXAMPLE VIII

(A) Starting Materials:

CKD - 40%, + Red Mud - 30%, + CaO - 20%, + Al_2O_3 - 10%,

(B) Calculated Chemical Constituents:

CaO - 42.8%, Al_2O_3 - 15.7%, SiO_2 - 5.3%, Fe_2O_3 - 14.5%, Na_2O - 0.7%.

This composition was a quick setting paste, but in remixing it turned muddy again. The cementitious properties were about the same as Examples VI and VII.

EXAMPLE IX

(A) Starting Materials:

CKD - 30%, + Red Mud - 30%, + CaO - 25% + Al_2O_3 - 15%,

(B) Calculated Chemical Constituents:

CaO - 42.7%, Al_2O_3 - 20.4%, SiO_2 - 4.4%, Fe_2O_3 - 14.3%, Na_2O - 0.7%.

Similar to as composition VII; quick set.

Compositions of CKD and Red Mud

For completeness, certain additional background information will be provided. In the foregoing specification, compositions for the CKD and Red Mud which were used in the foregoing examples, were given. The compositions given from other sources are also of interest, as showing that the compositions of CKD and Red Mud may differ significantly. More specifically in the following Tables XI and XII, two such alternate compositions are listed.

In retrospect, it is considered probable, that, with the addition of gypsum, firm cementitious action would have occurred with most of the compositions.

TABLE XI

CHEMICAL ANALYSIS OF CKD ACCORDING TO THE NATIONAL BUREAU OF STANDARDS

Table (1).

Constituent	Concentration %(*)	Certified values %
CaO	65.80	66.0
SiO_2	23.20	23.0
Al_2O_3	3.15	3.2
Fe_2O_3	1.72	1.8
SO_3	2.28	2.3
MgO	0.62	0.6
K_2O	0.22	0.25
TiO_2	0.21	0.21
Na_2O	0.13	0.15
SrO	0.08	0.09
P_2O_5	0.22	0.24
Mn_2O_3	0.06	0.06
F	0.04	0.04
ZnO	0.01	0.01
Cr_2O_3	0.01	0.01

(*) Weight percent

TABLE XII

TYPICAL ANALYSIS OF "MITSUI" RED MUD*

Oxide	Weight %	Average
Al_2O_3	19.1 ------ 22.4	20.6
Fe_2O_3	45.0 ------ 48.3	46.5
TiO_2	8.0 ------ 8.8	8.4
SiO_2	6.4 ------ 7.5	7.0
Na_2O	3.0 ------ 3.4	3.2
CaO	3.0 ------ 5.0	3.0
L.O.I		8.5

* From the proceedings of technical sessions sponsored by the TMS Light Metals Committee, Las Vegas, Nevada, February 24-28, 1980; "Light Metals", by Seishi Shimano et al.

TABLE XIII

COMPOSITION OF HIGH-IRON CEMENTS, PER MEHTA U.S. PATENT NO. 4,036,657

Potential compound composition wieght %				Oxide analysis wieght %					Compressive strength of cement paste 5-days (psi)
C_2S	C_4AF	$C_4A_3\bar{S}$	$C\bar{S}$	CaO	Al_2O_3	Fe_2O_3	SiO_2	SO_3	
40	25	20	15	51.1	15.3	8.2	14.0	11.4	12180
25	40	20	15	48.3	18.4	13.1	8.7	11.4	16240
0	70	20	10	43.8	24.7	23.0	0.0	8.5	11040
15	55	20	10	46.7	21.6	18.1	5.2	8.5	12560
27	51	15	7	49.5	18.2	16.8	9.4	6.1	12720
65	15	10	10	56.8	8.2	5.0	22.7	7.2	6150
55	15	20	10	54.2	13.2	5.0	19.2	8.5	11850
50	15	20	15	53.0	13.2	5.0	17.4	11.4	12130

TABLE XIV

	% by Weight
Si (as SiO_2)	19 - 21
Fe (as Fe_2O_3)	7 - 8
Ti (as TiO_2)	5 - 6
Al (as Al_2O_3)	25 - 27
Na (as Na_2O)	9 - 11
Ca (as CaO)	11 - 13
S (as SO_3)	2.0- 2.5
Loss on Ignition	14 - 16

ALCOA Red Mud

TABLE XV

	% by Weight
SiO_2	19 - 20
Fe_2O_3	7 - 9
TiO_2	5 - 6
Al_2O_3	7 - 9
Na_2O	5 - 7
CaO	42 - 46
SO_3	.3 - .6
Loss on Ignition	5 - 6

ALCOA "brown mud"

For completeness, in Table XIII the composition of a number of high iron cement compositions are set forth, in accordance with the Mehta patent cited hereinabove.

In Tables XIV and XV are some analyses of Red Mud (Table XIV) and brown mud (Table XV) which were courteously supplied by ALCOA, P. O. Box 300, Bauxite, Arkansas 72011. The Red Mud is filter cake from the filters used in deliquoring the Red Mud following a leaching process step. The brown mud sample is filter cake from rotary drain vacuum filters used for separating and washing the residue from leaching Red Mud/limestone/soad ash sinter.

EXAMPLE X

In this example and in Example XI set forth below, CKD as set forth in Table I was employed, and two types of Red Mud were used, that set forth in Table II and also brown mud (referred to in the present case generically as Red Mud) as included in Table XV.

In Example X the following materials were used: 40% CKD, 25% brown mud, 20% Red Mud, 15% $CaSO_4$, 10% Al_2O_3.

This corresponds in oxide weight percentages to the following:

CaO	39.9%
Al_2O_3	16.5%
SiO_2	9.7%
Fe_2O_3	11.8%
Na_2O	2.0%
SO_3	9.1%

The mixture was fired at 1200 degrees C. to 1250 degrees C., and was then ground in a ball mill for 14 hours. Two inch cubes of mortar were formed with the cement, and good cementitious action was found. The blocks are solid and very hard. The cubes were similar in color and appearance to light brown sugar. Detailed tests have not, however, been conducted on the blocks as

yet.

EXAMPLE XI

In Example XI, the following materials were used: 20% CKD, 20% Red Mud, 15% brown mud, 20% $CaSO_4$, 15% CaO, 10% Al_2O_3.

This corresponds in oxide weight percentages to the following:

CaO	42.0%
Al_2O_3	15.0%
SiO_2	6.0%
Fe_2O_3	10.5%
Na_2O	1.35%
SO_3	12.0%

The same treatment was followed as in Example X, and cast mortar cubes appeared to have much the same properties as those of Example X. Compression tests were made on two inch cubes after curing for one day or twenty-four hours in moist air; and the surprising result of compressive strength of about 2490 psi was realized, using ASTM test procedure C109. This figure is in the order of, or somewhat greater than the ultimate compressive strength of Portland cement. Incidentally, the color of the mortar cubes was that of dark chocolate.

In conclusion, it is noted that the foregoing specification relates to illustrative embodiments of the invention. It is to be understood that, in view of the varying composition of CKD and Red Mud, considerable variation in the composition of the cement and of the starting materials will still fall within the scope of the invention. For example, when the CKD or Red Mud has a higher calcium oxide content, less lime would need to be added; and similarly, when the alumina content of the Red Mud is high, less alumina would have to be added. Accordingly, the invention is not limited to the precise proportions in the examples set forth hereinabove.

What is claimed is:

1. A method of forming a high iron content cement comprising the steps of:

(1) preparing an intimate mixture including at least 20% Red Mud and 20% cement kiln dust, and a sulfur containing material; said mixture consisting essentially of between about 20% to 70% CaO, 5% to 35% Al_2O_3, 5% to 25% Fe_2O_3, 4% to 25% SO_3, and more than 0.5% but less than 10% of the combined oxides K_2O and Na_2O, with the foregoing percentage ranges being based on weight percentages of the indicated oxides;

(2) heating the combined constituents to an elevated temperature in the order of 1250 degrees C. to 1400 degrees C. to form clinker; and

(3) pulverizing the clinker to form a high iron content cement;

whereby a high strength, lightweight high iron content concrete structure is formed principally from waste materials.

2. A method as defined in claim 1 wherein said calcium oxide is included in said mixture in the form of lime.

3. A method as defined in claim 1 wherein said calcium oxide is included in said mixture in the form of dehydrated lime.

4. A method as defined in claim 1 wherein said sulfur containing compound is included in said mixture in the form of gypsum.

5. A method as defined in claim 1 when said sulfur containing compound is included in said mixture in the form of dehydrated gypsum.

6. A method for forming a concrete structure, including the steps as set forth in claim 1 and comprising the additional step of forming a steel reinforced concrete structure from said cement, wherein the enhanced bond between the high iron content material and the steel reinforcing provides a superior composite structure.

7. A high iron content cement made by the process of claim 1.

8. A method of forming a high iron content reinforced concrete structure comprising the steps of:

(1) manufacturing Portland type cement and retaining the cement kiln dust;

(2) extracting aluminum oxide from bauxite and retaining the residual Red Mud;

(3) preparing an intimate mixture including at least 20% of said Red Mud and 20% of said cement kiln dust, and a sulfur containing material; said mixture consisting essentially of between about 20% to 70% CaO, 5% to 35% Al_2O_3, 5% to 25% Fe_2O_3, 4% to 25% SO_3, and more than 0.5% but less than 10% of the combined oxides K_2O and Na_2O, with the foregoing percentage ranges being based on weight percentages of the indicated oxides;

(4) heating the combined constituents to an elevated temperature in the order of 1250 degrees C. to 1400 degrees C. to form clinker;

(5) pulverizing the clinker to form a high iron content cement;

(6) adding water to the cement and mixing with sand to form concrete;

(7) supplying the freshly mixed concrete into moulds containing steel reinforcing; and

(8) allowing the concrete to harden to form a reinforced concrete structure;

whereby a high strength, lightweight high iron content concrete structure is formed principally from waste materials, and wherein the concrete has an enhanced bond with the steel reinforcing.

9. A method as defined in claim 8 wherein the extracting of the aluminum oxide involves a leaching process.

10. A steel reinforced concrete structure made by the process of claim 8.

11. A high iron content cement comprising:

pulverized clinker of which the constituent components consist essentially of:

(1) Red Mud, 20% - 50%

(2) Cement Kiln dust, 20% - 50%

(3) Calcium Oxide, 5% - 25%

(4) Calcium Sulfate, 10% - 25%

(5) Alumina, 0% - 25% (to bring total alumina including that in the Red Mud and cement kiln dust to 10% to 35%).

12. A method of forming a high iron content cement comprising the steps of:

(1) preparing an intimate mixture including at least 20% Red Mud and 20% cement kiln dust, and a sulfur containing material; said mixture consisting essentially of between about 20% to 70% CaO, 5% to 35% Al_2O_3, 5% to 25% Fe_2O_3, and 4% to 25% SO_3, with the foregoing percentage ranges being based on weight percentages of the indicated oxides;

(2) heating the combined constituents to an elevated temperature in the order of 1250 degrees C. to 1400 degrees C. to form clinker; and

(3) pulverizing the clinker to form a high

iron content cement;

whereby a high strength, lightweight high iron content concrete structure is formed principally from waste materials.

13. A method as defined in claim 12 wherein said calcium oxide is included in said mixture in the form of lime.

14. A method as defined in claim 12 wherein said sulfur containing compound is included in said mixture in the form of gypsum.

15. A method as defined in claim 12 comprising the additional step of forming a steel reinforced concrete structure from said cement, wherein the enhanced bond between the high iron content material and the steel reinforcing provides a superior composite structure.

16. A high iron content cement made by the process of claim 12.

17. A method as defined in claim 12 wherein the mixture as prepared includes at least 20% Red Mud and 20% cement kiln dust, and a sulfur containing material; said mixture consisting essentially of between about 30% to 65% CaO, 10% to 25% Al_2O_3, 8% to 20% Fe_2O_3, 5% to 20% SO_3, and more than 0.5% but less than 10% of the combined oxides K_2O and Na_2O, with the foregoing percentage ranges being based on weight percentages of the indicated oxides.

18. A method of forming a high iron content cement comprising the steps of:

(1) preparing an intimate mixture including at least 20% Red Mud and 20% cement kiln dust, and a sulfur

containing material; said mixture consisting essentially of between about 32% to 40% CaO, 15% to 20% Al_2O_3, 10% to 16% Fe_2O_3, 10% to 15% SO_3, and 2% to 5% SiO_2, with the foregoing percentage ranges being based on weight percentages of the indicated oxides;

(2) heating the combined constituents to an elevated temperature in the order of 1250 degrees C. to 1400 degrees C. to form clinker; and

(3) pulverizing the clinker to form a high iron content cement;

whereby a high strength, lightweight high iron content concrete structure is formed principally from waste materials.

19. A method as defined in claim 18 comprising the additional step of forming a steel reinforced concrete structure from said cement, wherein the enhanced bond between the high iron content material and the steel reinforcing provides a superior composite structure.

20. A high iron content cement made by the process of claim 18.

21. A method as defined in claim 18 wherein said mixture as prepared includes more than 1% of the combined oxides of sodium and potassium.

22. A method as defined in claim 18 wherein said mixture as prepared includes more than 0.5 but less than 10% of the combined oxides of sodium and potassium.

23. A method of forming a high iron content cement comprising the steps of:

(1) preparing an intimate mixture consisting essentially of at least 20% Red Mud and 20% cement kiln dust, and at least 5% SO_3, with the foregoing percentages

being based on weight percentages of the indicated materials;

(2) heating the combined constituents to an elevated temperature in the order of 1250 degrees C. to 1400 degrees C. to form clinker; and

(3) pulverizing the clinker to form a high iron content cement;

whereby a high strength, lightweight high iron content concrete structure is formed principally from waste materials.

Fig. 1

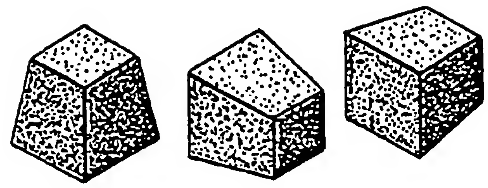


Fig. 2

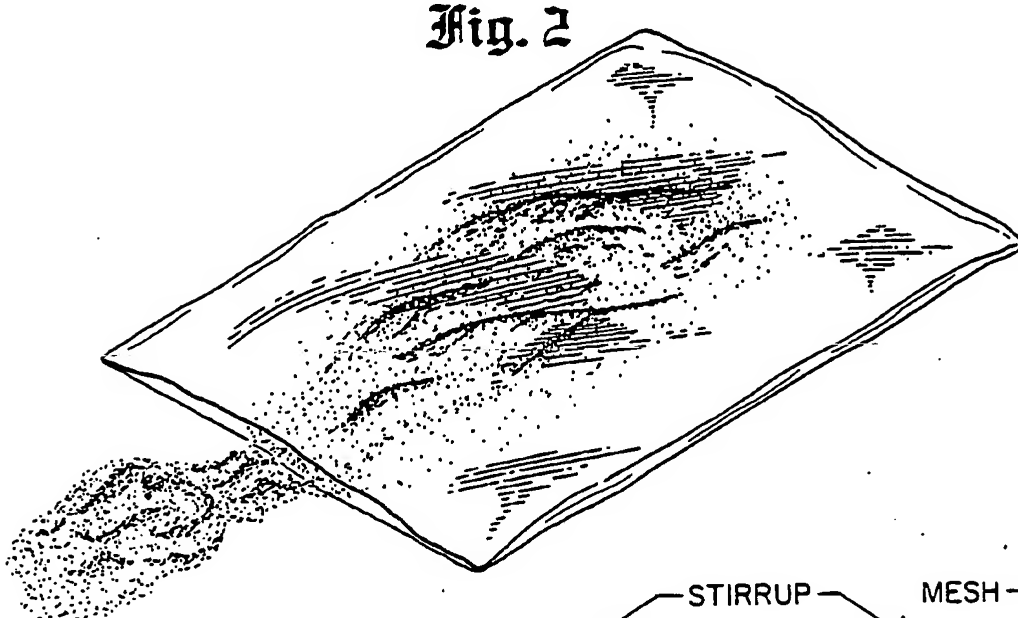


Fig. 4

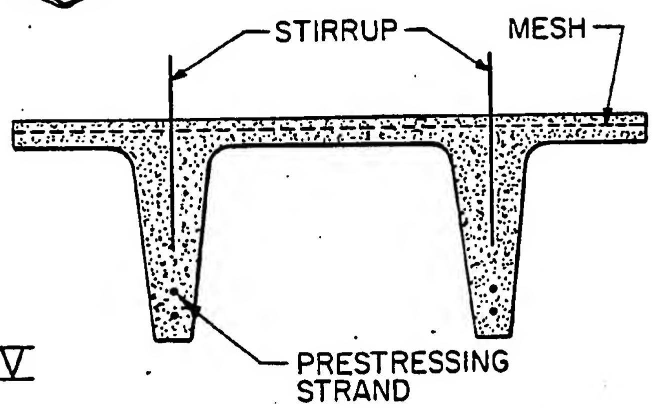
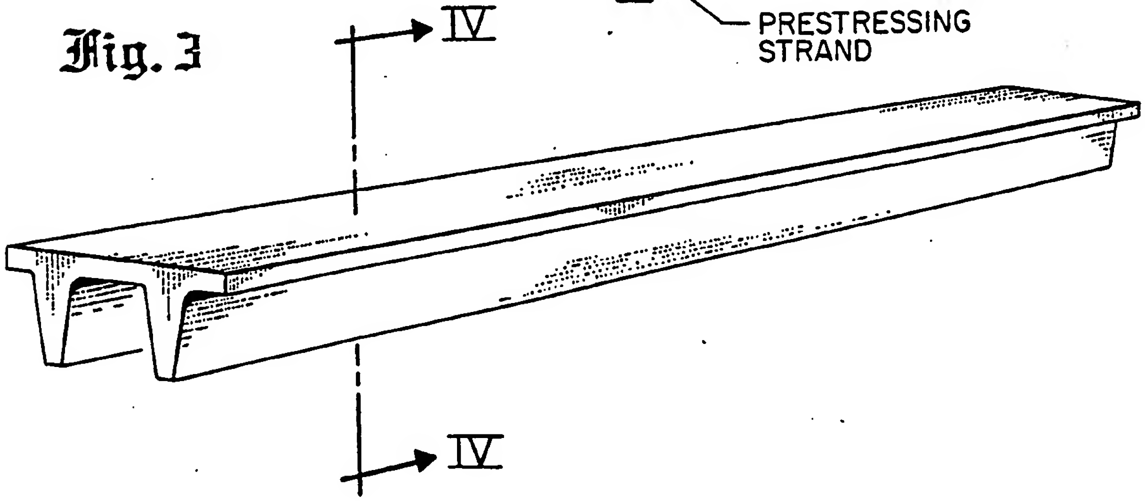


Fig. 3



INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/00671

I. CLASSIFICATI N OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL[4] C04B 07/22; 07/24; 07/48
U.S. CL 106/85

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	106/85; 89; 100; 103; 104

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	U.S., A, 4,036,657 PUBLISHED 19 JULY 1977, MEHTA , SEE COLUMNS 3 and 4.	1-23
A	U.S., A, 4,249,952 PUBLISHED 10 FEBRUARY 1981, DAVIS, JR. ET AL. SEE COL. 4, LINES 41-50.	1-23
A	U.S., A, 4,432,800 PUBLISHED 21 FEBRUARY 1984, KNELLER ET AL. SEE COL. 1, LINES 27-68.	1-23
A	S.U., A, 281,231 PUBLISHED 03 DECEMBER 1970, SEE COL.2, LINES 1-20.	1-23
A	S.U., A, 897,731 PUBLISHED 15 JANUARY 1982, SEE COL. 2, LINES 1-24.	1-23

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
14 MAY 1986	13 JUN 1986
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	STEVEN CAPELLA Steven Capella

WEST